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# Dissolution of Starch with Aqueous Ionic Liquid under Ambient Conditions

*Binjia Zhang<sup>a,b</sup>, Fengwei Xie<sup>\*b</sup>, Julia L. Shamshina<sup>c,d</sup>, Robin D. Rogers<sup>d</sup>, Tony McNally<sup>e</sup>, Peter J. Halley<sup>b</sup>, Rowan W. Truss<sup>b</sup>, Ling Chen<sup>f</sup>, Siming Zhao<sup>a</sup>*

<sup>a</sup> Key Laboratory of Environment Correlative Dietology (Ministry of Education), College of Food Science and Technology, Huazhong Agricultural University, Wuhan, Hubei 430070, China

<sup>b</sup> School of Chemical Engineering, The University of Queensland, Brisbane, Qld 4072, Australia

<sup>c</sup> 525 Solutions, Inc., 720 2nd Street, Tuscaloosa, AL 35401, USA

<sup>d</sup> Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 0B8, Canada

<sup>e</sup> International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK

<sup>f</sup> Guangdong Province Key Laboratory for Green Processing of Natural Products and Product Safety, South China University of Technology, Guangzhou, Guangdong 510640, China

KEYWORDS: Starch; Dissolution; Aqueous ionic liquid; 1-Ethyl-3-methylimidazolium acetate; Solvent effects

\* Corresponding Author. Email: f.xie@uq.edu.au, fwhsieh@gmail.com (F. Xie)

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4 ABSTRACT: With increased awareness of global sustainability, there has been growing interest  
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6 in the preparation of materials from natural, eco-friendly polymers (*i.e.*, biopolymers).  
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8 Nonetheless, despite their enormous application potential, biopolymers (starch, *etc.*) have a  
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10 native semi-crystalline structure with strong hydrogen bonding, and require use of solvents to  
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12 improve their processibility. However, the dissolution/processing of natural biopolymers such as  
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14 starch often requires heating and thus significant energy input. Herein, we report an aqueous  
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16 ionic liquid for fast and facile dissolution of starch, a typical semi-crystalline natural polymer,  
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18 under ambient conditions. The ionic liquid used is 1-ethyl-3-methylimidazolium acetate  
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20 ([C<sub>2</sub>mim][OAc]). In particular, it is revealed that 0.15:1 mol/mol [C<sub>2</sub>mim][OAc]:water mixture  
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22 disintegrates the sophisticated granule structure of native starch without apparently decreasing  
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24 the molecular mass within 1 h at room temperature (*i.e.*, 28 °C). In addition, this process did not  
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26 result in any undesired derivatization. The discovery of this phenomenon could provide guidance  
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28 for rationally designing ‘green’ processes for chemical and biological engineering for the  
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30 utilization of promising natural biopolymers.  
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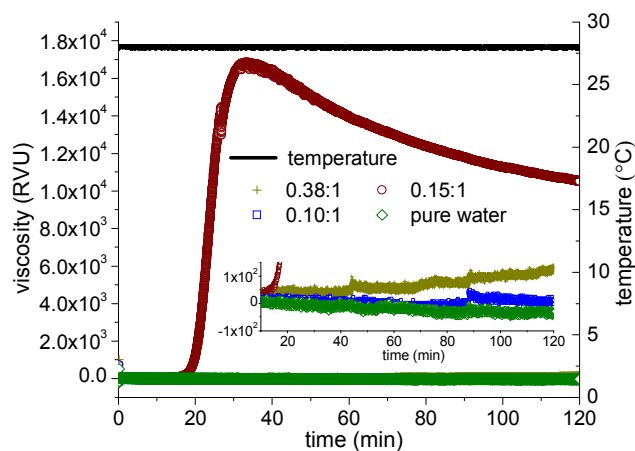
Currently, biopolymers are increasingly selected for reasons of global sustainability, as they are renewable, widely available, biodegradable and biocompatible.<sup>1</sup> Therefore, biopolymers have become important alternatives to petroleum-based polymers for fabricating eco-friendly materials. Starch, a semi-crystalline biopolymer in the native form of granules growing in plants, has attracted huge interest.<sup>2</sup> Considerable efforts have been devoted to improving the processes to convert starch into desirable forms<sup>3-4</sup> and thus to design starch-based materials.<sup>5-7</sup> However, the use of starch is often hindered by its low solubility in conventional solvents resulting from strong hydrogen bonding between starch chains within starch semi-crystalline structure. While the starch structure may be disrupted to some extent in excess water with significant energy input (*viz.* the “gelatinisation” process), there are always granule remnants in the gelatinised products.<sup>8</sup> Other solvents known for dissolving starch include dimethylsulfoxide (DMSO) containing LiBr,<sup>9</sup> and dimethylacetamide with LiCl.<sup>10</sup> These solvents, nonetheless, are toxic, and/or expensive, presenting drawbacks for the dissolution and modification of starch. Also, the dissolution of starch using these solvents still requires high temperatures and/or other special conditions. To address the sustainability issue, it is important to develop new solvents or processes that can transform starch into homogeneous amorphous forms with reduced energy consumption.

Recently, intense research has been focused on using ionic liquids (ILs) as alternative solvents for aiding biopolymer processing. ILs containing acetate [OAc]<sup>−</sup> or chloride [Cl]<sup>−</sup> anions and alkylimidazolium cations were identified most effective at dissolving biopolymers including starch.<sup>11-14</sup> Compared with mild [OAc]<sup>−</sup>, corrosive [Cl]<sup>−</sup> in an IL prominently depolymerises starch polymer chains, because of the acid hydrolysis of glycosidic bonds.<sup>15-16</sup> Consequently, acetate-based imidazolium ILs such as 1-ethyl-3-methylimidazolium acetate [C<sub>2</sub>mim][OAc] are recognised as excellent media for the dissolution and modification of starch.<sup>17-21</sup> [C<sub>2</sub>mim][OAc]

has a very low vapour pressure, high thermal stability and a relatively low viscosity at room temperature.<sup>22</sup> Nonetheless, significant energy (or heating) is still required to achieve a complete starch dissolution in pure [C<sub>2</sub>mim][OAc] or its water solutions.<sup>17, 23</sup>

Very recently, we found that the hydrogen bonding between starch hydroxyls and [OAc]<sup>−</sup> anions might be enhanced by addition of water in [C<sub>2</sub>mim][OAc],<sup>24</sup> though the amount of [OAc]<sup>−</sup> anions in the solvent was reduced by water. With inspiration of this finding, we hypothesised that aqueous [C<sub>2</sub>mim][OAc] at a certain concentration might dissolve starch even under ambient conditions. To this end, this work was focused on the effect of [C<sub>2</sub>mim][OAc] mixing with different amounts of water on the starch dissolution at room temperature (RT, *ca.* 28 °C). Regular maize starch, with an amylose content of 24.4 wt% and an initial moisture content of 13.36 wt%, was obtained from New Zealand Starch Ltd. (Onehunga, Auckland, New Zealand). [C<sub>2</sub>mim][OAc], of ≥ 95% purity with a moisture content of *ca.* 1200 ppm, was produced by IoLiTec Ionic Liquids Technologies GmbH (Salzstraße184, D-74076 Heilbronn, Germany). Milli-Q water was used in all instances. Table S1 (SI) shows the formulations of [C<sub>2</sub>mim][OAc]:water mixtures containing 10 wt% starch used in this work.

Here, we used aqueous [C<sub>2</sub>mim][OAc] as a solvent for the starch. Different [C<sub>2</sub>mim][OAc]:water ratios were used including 0:1 (pure water), 0.10:1, 0.15:1, and 0.38:1, mol/mol. It is known that the dissolution of native starch granules in a solvent could result in an increase in viscosity. Here, we studied the viscosity changes with time of the starch (10 wt%) in [C<sub>2</sub>mim][OAc]:water mixtures (Figure 1) using a Rapid Visco Analyser (RVA) 4 (Newport Scientific Pty Ltd., Warriewood, NSW 2102, Australia). Approximately 28 g of the biopolymer suspensions were contained in standard RVA canisters for viscosity measurements. The viscosity *vs.* time was recorded at 28 °C.

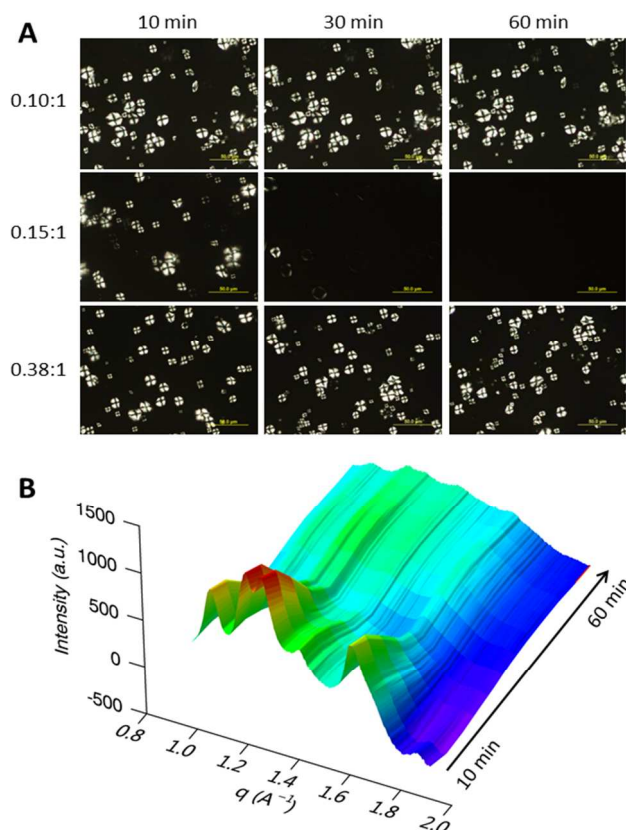


**Figure 1.** Viscosity profiles measured by a Rapid Visco Analyser (RVA) of 10 wt% starch (dry basis) in pure water (green rhombuses), and in 0.10:1 (blue squares), 0.15:1 (wine circles) and 0.38:1 (dark yellow crosses) mol/mol  $[C_2mim][OAc]$ :water mixtures at room temperature (28 °C). The viscosity in RVA is expressed in rapid visco units (RVU).

The viscosities of pure water and 0.10:1, 0.15:1 and 0.38:1 mol/mol  $[C_2mim][OAc]$ :water mixtures were *ca.* 0.1 RVU, 0.5 RVU, 0.9 RVU and 2.0 RVU, respectively, which would not change with time. As the dissolution time prolonged to 120 min, there was no apparent change in viscosity for up to 2 h for 10 wt% starch in pure water or 0.10:1 mol/mol  $[C_2mim][OAc]$ :water mixture from the initial viscosity of the suspension (25 RVU or 45 RVU, respectively). This constant viscosity suggested that at RT the starch structure could not be disrupted in pure water or 0.10:1 mol/mol  $[C_2mim][OAc]$ :water mixture. When 0.15:1 mol/mol  $[C_2mim][OAc]$ :water mixture was used for the starch, the initial viscosity was *ca.* 55 RVU, which started to rise rapidly at *ca.* 18 min, and at *ca.* 34 min the maximum of viscosity (*ca.* 16700 RVU) was achieved. This drastic viscosity change with time clearly showed the effectiveness of the 0.15:1 mol/mol mixture to rapidly disorganise native starch granules at RT. The starch molecules liberated from the compact native granules dramatically increased the viscosity of the solution.

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3 Interestingly, a further increase in the [C<sub>2</sub>mim][OAc]:water ratio from 0.15:1 to 0.38:1 mol/mol  
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5 did not enhance the destructure of starch. The treatment with the 0.38:1 mol/mol mixture for  
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7 120 min just slightly increased the system viscosity from *ca.* the initial value of *ca.* 70 RVU to  
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9 *ca.* 120 RVU. Thus, the 0.15:1 mol/mol [C<sub>2</sub>mim][OAc]:water mixture performed most  
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11 effectively for rapidly dissolving starch under ambient conditions.  
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15 The native starch structure has a hierarchical organisation containing crystallites and semi-  
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17 crystalline lamellae. To check the effect of the aqueous [C<sub>2</sub>mim][OAc] on the crystallites, we  
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19 further studied polarised light images and time-resolved wide-angle X-ray scattering (WAXS)  
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21 patterns for the starch (10 wt%) during dissolution in the 0.15:1 mol/mol mixture at RT  
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23 (Figure 2). In the initial period (10 min) of dissolution, the starch displayed strong birefringence  
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25 (Figure 2A) and WAXS peaks (Figure 2B). However, both the birefringence and WAXS  
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27 intensities were rapidly weakened with the increased dissolution time; and they completely  
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29 disappeared within 60 min. Moreover, the 2D SAXS patterns (Figure S1, SI) revealed that the  
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31 typical scattering circle for the semi-crystalline lamellar structure of starch on the nanoscale  
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33 became invisible after treatment with the 0.15:1 mol/mol mixture for 60 min. All these results  
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35 clearly indicated the 0.15:1 mol/mol mixture could easily destroy and dissolve the native starch  
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37 structure.  
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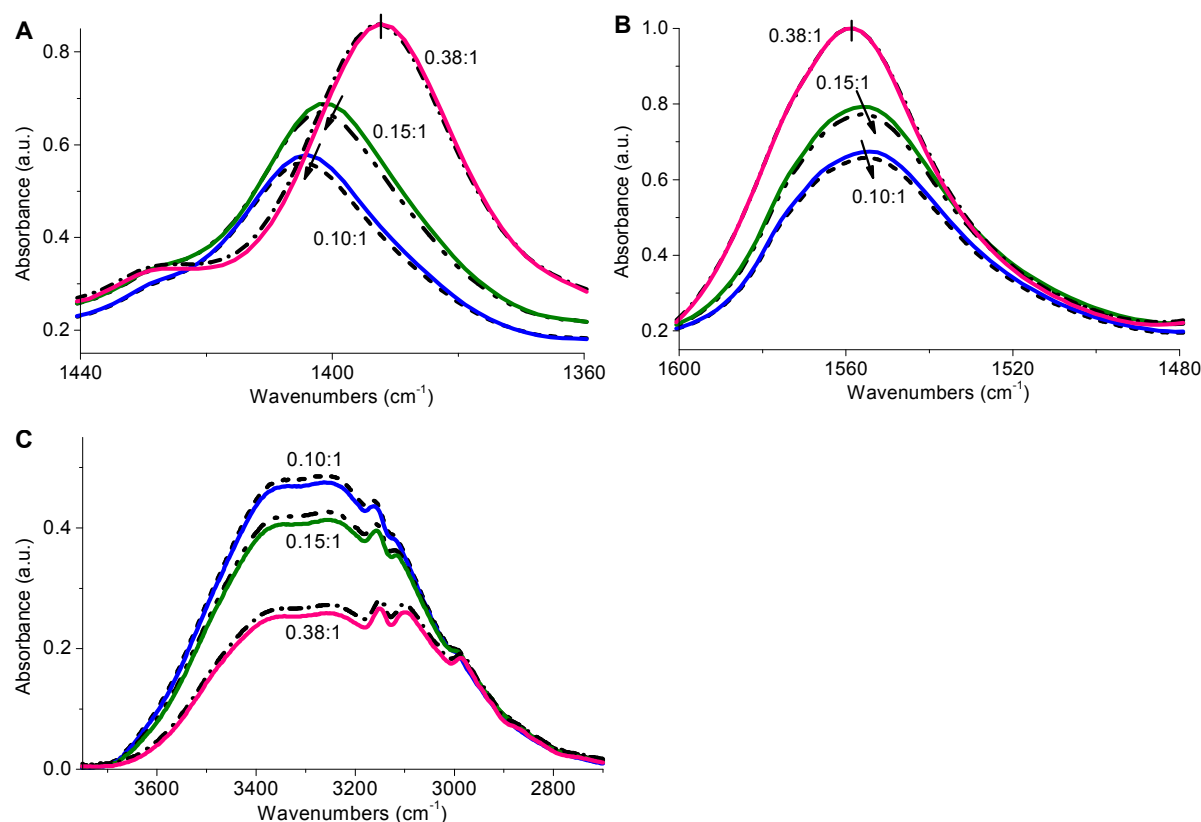


**Figure 2.** Polarised-light micrographs (A) of 10 wt% starch (dry basis) in 0.10:1, 0.15:1 and 0.38:1 mol/mol  $[\text{C}_2\text{mim}][\text{OAc}]$ :water mixtures at room temperature (28 °C); Time-resolved WAXS pattern (B) of 10 wt% starch (dry basis) in 0.15:1 mol/mol  $[\text{C}_2\text{mim}][\text{OAc}]$ :water mixture at room temperature (28 °C).

To help understanding the mechanism of starch dissolution at RT, the attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of  $[\text{C}_2\text{mim}][\text{OAc}]$ :water mixtures and those containing 10 wt% starch are shown in Figure 3. Two intense and broad IR absorption peaks at  $1390\text{--}1405\text{ cm}^{-1}$  and at  $1550\text{--}1560\text{ cm}^{-1}$  were observed for the  $[\text{OAc}]^-$  anion in the  $[\text{C}_2\text{mim}][\text{OAc}]$ :water mixtures (Figure 3A and B). These peaks were ascribed to the symmetric and asymmetric O–C–O stretching, respectively.<sup>24-25</sup> At low IL concentrations (*i.e.*, 0.10:1 and 0.15:1 mol/mol  $[\text{C}_2\text{mim}][\text{OAc}]$ :water), the addition of starch led to slight reductions in intensity



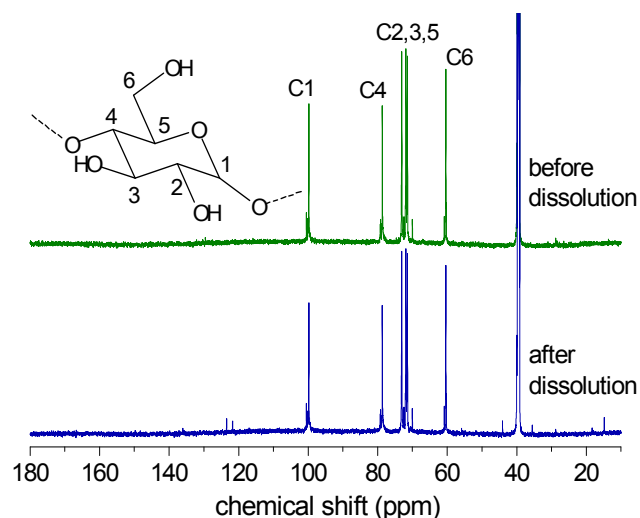
and small shifts in position for the two acetate stretches. These changes were confirmed with repeated tests and indicated that the acetate ions interacted with the starch hydroxyl groups *via* hydrogen bonding<sup>24</sup> at RT and weakened the [C<sub>2</sub>mim][OAc]-water interactions. Also, the hydration of [OAc]<sup>−</sup> weakened the kosmotropic effect of this anion on its interaction with a polyol hydrogen bond network.<sup>26</sup> Consequently, the addition of starch to the [C<sub>2</sub>mim][OAc]:water mixture increased the water hydroxyl stretching at *ca.* 3400 cm<sup>−1</sup> (Figure 3), resulting from the weakened solvation of [OAc]<sup>−</sup> with water molecules. It was noteworthy that in the 0.38:1 mol/mol mixture, there was no change observed for the acetate stretches contrary to those in 0.10:1 and 0.15:1 mol/mol mixtures. Further investigation is needed to understand the interactions between starch, the IL and water in this tertiary system.



**Figure 3.** FTIR spectra for 0.10:1, 0.15:1 and 0.38:1 mol/mol [C<sub>2</sub>mim][OAc]:water mixtures before (real line) and after (dash line) adding 10 wt% starch (dry basis) at room temperature (28 °C) for 60 min.

Aqueous NaOH solution is known as a cheap solvent for starch.<sup>27</sup> Nonetheless, a strict control of conditions is required for the starch dissolution, including the use of a very low NaOH concentration (*e.g.* 2%, w/v), low temperature (35 °C) and a very long time ( $\geq 7$  days). Even so, only a small amount of starch (*e.g.* 1.5 wt% and 2 wt%) can be dissolved. These drawbacks restrict the alkali solution from being used as a solvent for starch. In contrast, our work demonstrated that 0.15:1 mol/mol [C<sub>2</sub>mim][OAc]:water mixture could easily dissolve an evidently higher amount (*e.g.* 10 wt%) of starch under ambient conditions.

We also checked the chemical difference of the starch before and after dissolution at 10 wt% in 10 mL 0.15:1 mol/mol [C<sub>2</sub>mim][OAc]:water mixture at RT. After dissolution for 60 min, the starch was regenerated by 20 mL of ethanol. The resulted starch was washed with 10 mL of water and then 20 mL of ethanol, followed by filtration, for three times. The solution <sup>13</sup>C nuclear magnetic resonance (NMR) spectra for the starch before and after dissolution exhibited the same resonance peaks between 100 to 60 ppm, which originated from the carbons of starch glucan units (Figure 4). The dissolved starch also had very weak resonances especially at *ca.* 15, 36, 44, 122, and 124 ppm, corresponding to the C8', C3', C7', C6', and C5' of [C<sub>2</sub>mim][OAc], respectively (see Figure S2, SI). These weak resonances indicated the presence of a slight amount of IL residue in the regenerated starch after washing for three times, as also shown by the solution <sup>1</sup>H NMR spectra in Figure S3 in SI. Thus, the solvent did not induce any derivatisation of starch during the dissolution process at RT. The absence of starch derivatisation was further confirmed by FTIR and Raman spectroscopic analyses (see Figure S4, SI).



**Figure 4.** Solution  $^{13}\text{C}$  NMR spectra of starch before and after dissolution at 10 wt% (dry basis) in 0.15:1 mol/mol  $[\text{C}_2\text{mim}][\text{OAc}]$ :water mixture at room temperature (28 °C) for 60 min in  $\text{DMSO}-d_6$ .

A very recent finding shows that heating pure  $[\text{C}_2\text{mim}][\text{OAc}]$  with cellulose, another polysaccharide, at a high temperature (*e.g.* 120 °C) for an extended time (*e.g.* 48 h) transforms a certain proportion of  $[\text{C}_2\text{mim}]^+$  into an imidazolium adduct 1-ethyl-2-(hydroxymethyl)-3-methylimidazolium ( $[\text{C}_2\text{C}_1(\text{HO})\text{C}_1^2\text{im}]^+$ ).<sup>28</sup> This transformation potentially hinders the complete dissolution of cellulose but can be suppressed at a reduced temperature. Therefore, the dissolution under modest conditions (at RT for a short time) could serve as a strategy to dissolve polysaccharides without undesired derivatisation.

To understand the molecular structure of starch before and after dissolution, we further used gel permeation chromatography coupled with multi-angle light scattering (GPC-MALS) (Figure S5). It was revealed that the molar mass profile showed very slight variations for the starch before and after dissolution at 10 wt% in 0.15:1 mol/mol  $[\text{C}_2\text{mim}][\text{OAc}]$ :water mixture at RT. Specifically, there was no apparent change in the molar mass distribution of the starch after

dissolution, indicating the negligible molecular degradation of the starch. This result was somewhat different from a previous report where certain molecular degradation of starch occurred during dissolution in pure [C<sub>2</sub>mim][OAc] or its aqueous forms on dynamic heating from 20 °C to 120 °C.<sup>17</sup> Our results here suggested that 0.15:1 mol/mol [C<sub>2</sub>mim][OAc]:water mixture could be used for facile and rapid dissolution of starch at RT with minimal molecular degradation.

In summary, aqueous [C<sub>2</sub>mim][OAc] could disrupt semi-crystalline starch at RT. In particular, 0.15:1 mol/mol [C<sub>2</sub>mim][OAc]:water mixture effectively dissolved starch under ambient conditions, without derivatisation and apparent degradation of starch. The discovery here could be helpful for rationally designing ‘green’ chemical and biological engineering processes for the processing of natural polymers. More research, *e.g.*, the dissolution kinetics, the molecular interactions of starch-IL-water, is underway for in-depth understanding the dissolution of starch with aqueous [C<sub>2</sub>mim][OAc] at RT.

## ASSOCIATED CONTENT

**Supporting Information (SI)** is available free of charge on the ACS Publications website at DOI: xxx. See SI for Experimental details, and supplementary Table and Figures.

## AUTHOR INFORMATION

### Corresponding Author

\* Fengwei Xie. Email: f.xie@uq.edu.au, fwhsieh@gmail.com

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

IL, ionic liquid; [C<sub>2</sub>mim][OAc], 1-ethyl-3-methylimidazolium acetate; DMSO, dimethylsulfoxide; RVA, Rapid Visco Analyser; WAXS, wide-angle X-ray scattering; SAXS, small-angle X-ray scattering; ATR-FTIR, attenuated total reflectance-Fourier transform infrared; NMR, nuclear magnetic resonance; GPC-MALS, gel permeation chromatography coupled with multi-angle light scattering.

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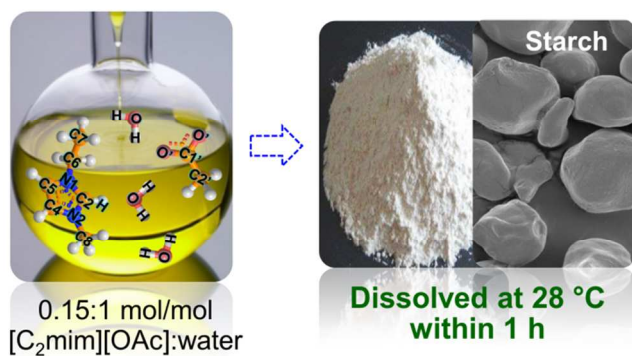


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# Dissolution of Starch with Aqueous Ionic Liquid under Ambient Conditions

*Binjia Zhang<sup>a,b</sup>, Fengwei Xie<sup>\*b</sup>, Julia L. Shamshina<sup>c,d</sup>, Robin D. Rogers<sup>d</sup>, Peter J. Halley<sup>b</sup>, Tony McNally<sup>e</sup>, Rowan W. Truss<sup>b</sup>, Ling Chen<sup>f</sup>, Siming Zhao<sup>a</sup>*



An aqueous ionic liquid (1-ethyl-3-methylimidazolium acetate, [C<sub>2</sub>mim][OAc]) is reported for fast and facile dissolution of a natural biopolymer, *i.e.*, starch, under ambient conditions.